

Theoretical modelling of CD and ORD spectra of suspensions with large nonspherical particles

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Abstract

The paper is devoted to the theoretical investigation of the circular dichroism (CD) and optical rotatory dispersion (ORD) spectra of turbid layers with large particles of arbitrary shapes. The cases of oriented cylinders and spheroids are considered in detail. It is assumed that the optical thickness of layers is low and the refractive index of scatterers is close to the refractive index of a host medium, which is usually the case for bio-liquids.

It is found that the simple correction function allows to transform CD and ORD spectra measured for turbid layers to that of particles. This result could be of importance for studies of living cells molecular structure changes during their life cycles.

Keywords: Circular dichroism, optical rotation dispersion, light scattering

1. Introduction

Circular dichroism (CD) and optical rotation dispersion (ORD) spectra are sources of information on asymmetry of molecular structures. For instance, this asymmetry is an important feature of living cells. The CD and ORD spectra are used in organic chemistry as a routine tool in stereochemical analysis.

In most cases chiroptical spectroscopy (CS) is applied to substances in solution. However, biological media are usually highly inhomogeneous due to the presence of various macroscopic particles (e.g., red blood cells). Thus, there is a task of generalization of the CS on the case of particulate media. Some results in this direction have already been reported [1, 2].

The major result is that CD and ORD spectra of substances inside small particles may differ substantially from spectra measured for dispersed layers. They depend on the refractive indices of particles, their size (and, possibly, on the concentration of particles, if the optical thickness of a sample is high). The case of chiral spheres can be treated in the framework of exact electromagnetic scattering theory [1].

However, most biological particles are nonspherical in shape. So, the generalization should be done, allowing for nonspherical shapes of particles in an optically active turbid layer. This can be achieved in two ways. The first is to use known solutions of electromagnetic scattering problems for chiral cylinders and spheroids [3, 4]. The second is to apply the approximate scattering theories (e.g., the Rayleigh, Rayleigh–Gans, discrete dipoles and anomalous diffraction approximations [1, 2, 5]). Here we will use the second approach, namely the anomalous diffraction theory (ADT) of van de Hulst [5].

This is mostly due to the following reasons. Firstly, the ADT is perfectly suitable for the solution of applied problems due to its intrinsic mathematical simplicity. Secondly, the range of shapes which can be considered is wide. This is not the case for the exact electromagnetic scattering solutions. In fact, solutions of the wave equation for most particle shapes occurring in nature has not been derived due to the mathematical complexity involved. The important thing is that the accuracy of approximate equations can be far better than the accuracy of experiments performed. Clearly, it depends on

the correspondence of particle parameters in the experiment to the range of applicability of the approximate theory.

For instance, it was obtained [1] that an additional multiplier is needed to account for the light scattering effects in the chiroptical spectroscopy of disperse media with particles, which are much smaller than the wavelength λ of the incident light. The case of arbitrarily shaped particles at $kd|\bar{m} - 1| \ll 1$, $|\bar{m} - 1| \ll 1$ (d is the maximal size of particles, $k = 2\pi/\lambda$, $\bar{m} = (m_L + m_R)/2$, m_L and m_R are refractive indices for left-handed and right-handed circularly polarized waves correspondingly) was studied by Bohren [6]. It was found that light scattering effects can be neglected in this particular case. Correspondingly, CD and ORD spectra of substances inside such particles coincide with spectra measured for dispersed layers (in the framework of the single scattering approximation, of course). This allows us to use the CS, developed for homogeneous media, in the case of particulate media.

Clearly, the CD and ORD spectra of turbid layers are not equal to CD and ORD spectra of particles substances if the condition $kd|\bar{m} - 1| \ll 1$ is not satisfied (either due to the small value of the wavelength λ or large values of d). The aim of this paper is to consider this discrepancy for the case of large ($kd \gg 1$) optically soft ($|\bar{m} - 1| \ll 1$) nonspherical particles, where the van de Hulst approximation [5] can be used.

2. CD and ORD spectra of turbid layers with nonspherical particles

Let us assume that the optical thickness of a medium in question is low, which allows us to neglect the contribution of multiply scattered photons. Then the disperse medium can be considered (at least as far as the light transmission is concerned) as an effectively homogeneous medium with the 'effective' refractive index [1, 5]:

$$M = 1 - 2\pi i N k^{-3} S(0) \quad (1)$$

where N is a number of particles in a unit volume and $S(0)$ is the so-called amplitude scattering function in the forward direction. Clearly, this equation can be applied only at small values of $|M - 1|$. Equation (1) is easily generalized for the case of disperse media with optically active particles. Namely, two refractive indices are introduced in this case: M_1 —for left-handed circularly polarized waves and M_2 —for right-handed circularly polarized waves. The values of M_1 and M_2 coincide for isotropic nonchiral particles. They generally differ for optically active particles. This difference is usually small ($|M_1 - M_2| \ll 1$). Nevertheless, it is detectable and can be used to study molecular asymmetries of substances inside small light scattering globules. Thus, it follows [1]:

$$M_j(\lambda) = 1 - 2\pi i N k^{-3} S_j(\lambda) \quad (2)$$

and by definition [1]

$$\varphi(\lambda) = \frac{\pi}{\lambda} \text{Re}(M_1(\lambda) - M_2(\lambda)) \quad (3)$$

$$\theta(\lambda) = \frac{\pi}{\lambda} \text{Im}(M_1(\lambda) - M_2(\lambda)) \quad (4)$$

where $\varphi(\lambda)$ and $\theta(\lambda)$ are ORD and CD spectra per unit length of a sample.

Let us introduce the complex number:

$$\Psi(\lambda) = \varphi(\lambda) - i\theta(\lambda). \quad (5)$$

Then it follows from equations (2)–(5):

$$\Psi(\lambda) = \frac{i\pi N}{k^2} \Delta S(\lambda) \quad (6)$$

where

$$\Delta S(\lambda) = S_2(\lambda) - S_1(\lambda). \quad (7)$$

Thus, the problem of the calculation of CD and ORD spectra of a turbid layer is reduced to the calculation of the difference $\Delta S(\lambda)$. The value of $\Delta S(\lambda)$ is small due to the small difference $\Delta m(\lambda) = m_L(\lambda) - m_R(\lambda)$. It follows due to this fact:

$$S'(\lambda) = \left. \frac{\partial S}{\partial m} \right|_{m=\bar{m}} = \frac{\Delta S(\lambda)}{\Delta m(\lambda)}. \quad (8)$$

Substituting equation (8) into (6), one obtains:

$$\Psi(\lambda) = \frac{2\pi}{ik^3 V} S'(\lambda) \Psi_0(\lambda) \quad (9)$$

where V is the average volume of particles,

$$\Psi_0(\lambda) = \varphi_0(\lambda) - i\theta_0(\lambda) \quad (10)$$

$$\varphi_0(\lambda) = \frac{\pi c}{\lambda} \text{Re}(m_L(\lambda) - m_R(\lambda)) \quad (11)$$

$$\theta_0(\lambda) = \frac{\pi c}{\lambda} \text{Im}(m_L(\lambda) - m_R(\lambda)) \quad (12)$$

and $c = NV$ is the volumetric concentration of particles. One can see from equation (9) that initial spectra $\Psi_0(\lambda) = \varphi_0(\lambda) - i\theta_0(\lambda)$ indeed change and this change is due to spectral variation of the function $\lambda^3 S'(\lambda)$.

Thus, the main task now is to calculate the dependence $S(\lambda)$ and then to consider the derivative $S'(\lambda)$. For this, we need to make some assumptions. In particular, we will assume, as it is usually done in the framework of the anomalous diffraction approximation [5], that particles are optically soft ($|\bar{m} - 1| \ll 1$) and large ($kd \gg 1$). Then the function $S(\lambda)$ can be found in the framework of the van de Hulst (or anomalous diffraction) approximation [5]:

$$S(\lambda) = \frac{k^2}{2\pi} \int_{\Sigma} (1 - \exp(-i\sigma(p))) dp \quad (13)$$

where Σ is the projection of a particle on the plane perpendicular to the incident light and $\sigma(p) = kl(\bar{m} - 1)\xi(p)$ is the phase shift of a ray on the length $l\xi(p)$ where the parameter $l = V/\Sigma$ is introduced for the further convenience. Equation (13) can be applied only to the case of identical particles with a fixed orientation. For more complex cases, one should use values $\langle S(\lambda) \rangle$ averaged over the particle's dimensions and orientations. It follows from equation (13) for the derivative

$$S'(\lambda) = \frac{ik^3 l}{2\pi} \int_{\Sigma} \xi(p) \exp[-ik(\bar{m} - 1)l\xi(p)] dp. \quad (14)$$

Thus, one can obtain from equations (9), (14):

$$\Psi(\lambda) = H(\lambda)\Psi_0(\lambda) \quad (15)$$

where

$$H(\lambda) = \int_S \xi(q) \exp(-i\rho\xi(q)) dq \quad (16)$$

where $q = p/\Sigma$, $\rho = kl(\bar{m} - 1)$, and S is the unit area. The shape of this unit area coincides with the shape of the particle projection. It follows from equation (15)

$$\Psi_0(\lambda) = \frac{\Psi(\lambda)}{H(\lambda)}. \quad (17)$$

Thus, the knowledge of the function $H(\lambda)$ allows us to find the intrinsic spectrum $\Psi_0(\lambda)$ of particles from the measured spectrum $\Psi(\lambda)$. It is known, however, that $H(\lambda) \rightarrow 1$ as $\rho \rightarrow 0$ [6]. This means that

$$\Upsilon \equiv \int_S \xi(q) dq = 1. \quad (18)$$

This equality holds for any particle shape.

The function $H(\lambda)$ for a given particle size, shape and orientation can be calculated numerically or analytically in some cases (see below). For numerical integration, one should find the length $L(q) = l\xi(q)$ of a light ray inside the particle. After that the integration (16) can be performed for a particle of an arbitrary shape. As a matter of fact, a three-dimensional particle is replaced by a two-dimensional amplitude-phase screen in the framework of the van de Hulst approximation [5]. Thus, the main task is to find the phase shift distribution on that screen.

3. Cylinders

Let us now consider the case of cylindrical particles. We will assume that tops of cylinders are oriented normally to the incident light beam. The transverse cross section of a cylinder can be arbitrary. Clearly, for the illumination of the cylinder along the symmetry axis all phase shifts are equal and the equivalent amplitude-phase screen has a constant value of the phase shift. Then it follows: $\xi \equiv 1$ and

$$\rho = kL(\bar{m} - 1) \quad (19)$$

where L is the length of the cylinder. We obtain from equation (16):

$$H(\lambda) = \exp(-i\rho(\lambda)) \quad (20)$$

where we accounted for the fact that $\xi(q) \equiv 1$ in this case. It follows from equation (15)

$$\Psi(\lambda) = \Psi_0(\lambda) \exp(-i\rho(\lambda)). \quad (21)$$

Then we have from equation (21) (in correspondence with [6]) as $\rho(\lambda) \rightarrow 0$:

$$\Psi(\lambda) \equiv \Psi_0(\lambda). \quad (22)$$

However, at larger values of $\rho(\lambda)$ considerable differences between spectra $\Psi(\lambda)$ and $\Psi_0(\lambda)$ occur.

In particular, it follows (see equation (21)):

$$\varphi(\lambda) = \varphi_0(\lambda) \cos \rho(\lambda) - \theta_0(\lambda) \sin \rho(\lambda) \quad (23)$$

$$\theta(\lambda) = \varphi_0(\lambda) \sin \rho(\lambda) + \theta_0(\lambda) \cos \rho(\lambda) \quad (24)$$

if particles are not absorbing. It follows at $\rho(\lambda) = 2\pi n$ ($n = 0, 1, 2, 3, \dots$):

$$\varphi(\lambda) \equiv \varphi_0(\lambda) \quad \theta(\lambda) \equiv \theta_0(\lambda). \quad (25)$$

However, one obtains at $\rho(\lambda) = \pi(n + \frac{1}{2})$ ($n = 0, 2, 4, 6, 8$):

$$\varphi(\lambda) = -\theta_0(\lambda) \quad \theta(\lambda) = \varphi_0(\lambda). \quad (26)$$

Equations (23), (24) allow to consider the distortion of spectra for arbitrary phase shifts $\rho(\lambda)$.

4. Ellipsoids

Let us consider now the case of oriented ellipsoidal particles. The function $\xi(q)$ for this case was found by Lopatin and Sidko [7]. It has the following simple form [7]:

$$\xi(q) = \frac{3}{2}\sqrt{1-q}. \quad (27)$$

It follows from equations (16), (27):

$$H(\lambda) = \frac{3}{2} \int_0^1 \sqrt{1-q} \exp(-i\rho\sqrt{1-q}) dq \quad (28)$$

where

$$\rho = kd(\bar{m} - 1) \quad d = \frac{3}{2}l. \quad (29)$$

For spheres the value of d coincides with the diameter. It follows from equation (28) after integration:

$$H(\lambda) = \frac{6i(1 - e^{-i\rho})}{\rho^3} + \frac{6e^{-i\rho}}{\rho^2} + \frac{3ie^{-i\rho}}{\rho}. \quad (30)$$

We obtain from equation (30) as $\rho \rightarrow 0$:

$$H(\lambda) = (1 - \frac{3i}{4}\rho - \frac{3}{10}\rho^2).$$

One can see again that $H \rightarrow 1$ as $\rho \rightarrow 0$ as it should be [6].

The value of $H(\lambda)$ in equation (30) can be presented in the following form

$$H(\lambda) = u(\lambda) - iv(\lambda) \quad (31)$$

where

$$u(\lambda) = \frac{3 \sin \rho}{\rho} + \frac{6 \cos \rho}{\rho^2} - \frac{6 \sin \rho}{\rho^3} \quad (32)$$

$$v(\lambda) = -\frac{3 \cos \rho}{\rho} + \frac{6 \sin \rho}{\rho^2} - \frac{6(1 - \cos \rho)}{\rho^3} \quad (33)$$

and we assume that particles are nonabsorbing. Then we have:

$$\varphi(\lambda) = u(\lambda)\varphi_0(\lambda) - v(\lambda)\theta_0(\lambda) \quad (34)$$

$$\theta(\lambda) = v(\lambda)\varphi_0(\lambda) + u(\lambda)\theta_0(\lambda) \quad (35)$$

which is similar to equations (23), (24). Generally speaking, linear relationships (34), (35) hold for any particle shape. However, the specific dependencies $u(\lambda)$ and $v(\lambda)$ differ depending on the specific shape of particles. We present functions $u(\lambda)$ and $v(\lambda)$ for cylinders and ellipsoids in figures 1 and 2. One can see that multipliers $H(\lambda)$ for cylinders and ellipsoids differ considerably. In particular, it follows that $u \rightarrow 0$, $v \rightarrow 0$ as $\rho \rightarrow \infty$ for ellipsoids. This is not the case for oriented cylinders. In practice, of course, there is

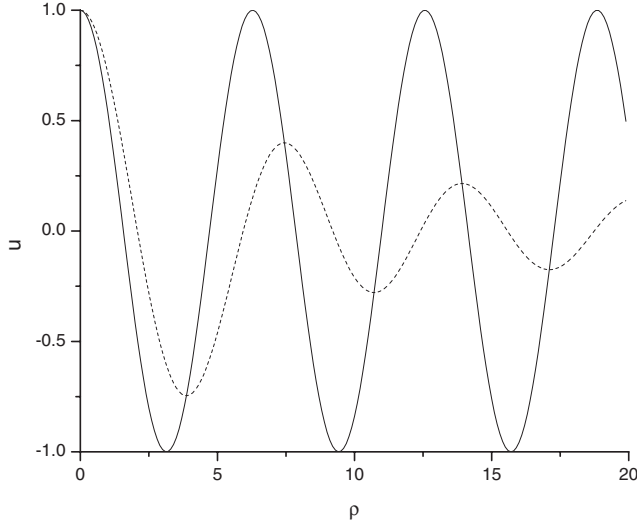


Figure 1. The dependence of the function u on the phase shift ρ for cylinders (solid curve) and ellipsoids (broken curve).

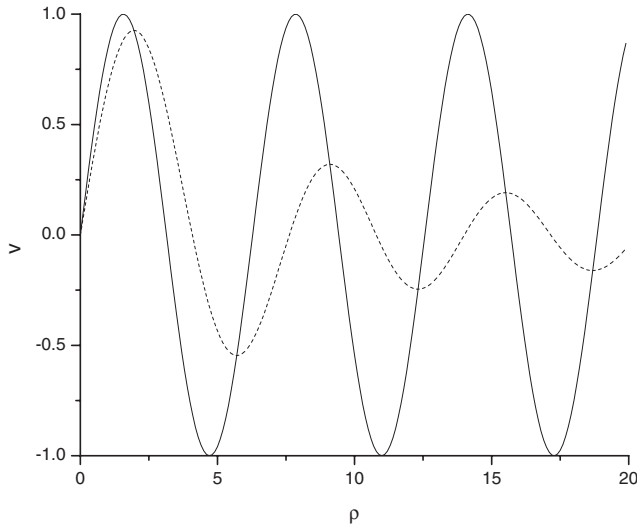


Figure 2. The same as in figure 1, but for the function $v(\rho)$.

some absorption of light inside particles. This will lead to the damping of oscillations both for cylinders and spheroids.

For illustrative purposes we present spectra $\varphi(\lambda)$ and $\theta(\lambda)$, obtained with equations (32)–(35) for different values of the parameter $b = 2\pi d(\bar{m} - 1)$ in figures 3 and 4. Note, that we neglected the imaginary part of \bar{m} in calculations of the parameter $b \equiv \lambda\rho$. Also we neglected possible variations of b with λ . Spectra $\Delta n(\lambda) = \text{Re}(\Delta m(\lambda))$ and $\Delta\chi(\lambda) = \text{Re}(\Delta m(\lambda))$, which close to those of the poly-L-glutamic acid, were taken from [8]. Then we used equations (11), (12) to find $\varphi_0(\lambda)$ and $\theta_0(\lambda)$. The concentration of particles c was assumed to be equal 0.001. Finally, we expressed $\varphi_0(\lambda)$ and $\theta_0(\lambda)$ in degrees, multiplying (11) and (12) by $180/\pi$. The thickness of a dispersed layer was assumed to be equal 1 mm. We see that the parameter b , which is proportional to the phase shift of a ray on the maximal dimension of a particle has a paramount importance for spectra $\varphi(\lambda)$ and $\theta(\lambda)$. At small values of b spectra of dispersed layers are very close to those of molecular solution of poly-L-glutamic acid. This is in a full accordance with data presented in [6]. However, they differ considerably from initial spectra $\varphi_0(\lambda)$ and $\theta_0(\lambda)$ for large values of b .

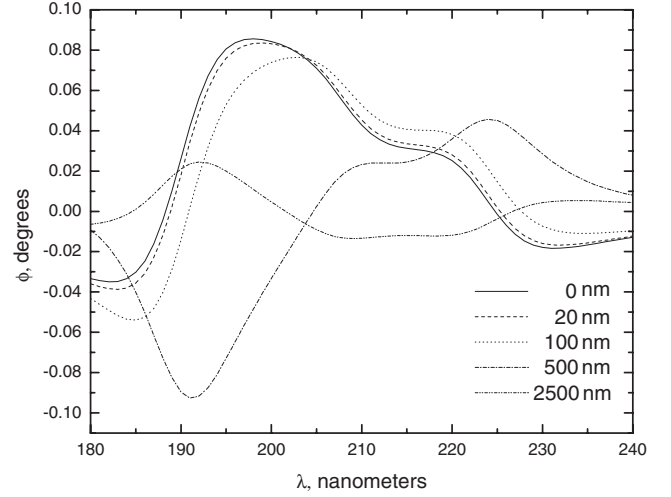


Figure 3. Spectra $\varphi(\lambda)$ at $b = 0, 20, 100, 500$ and 2500 nm.

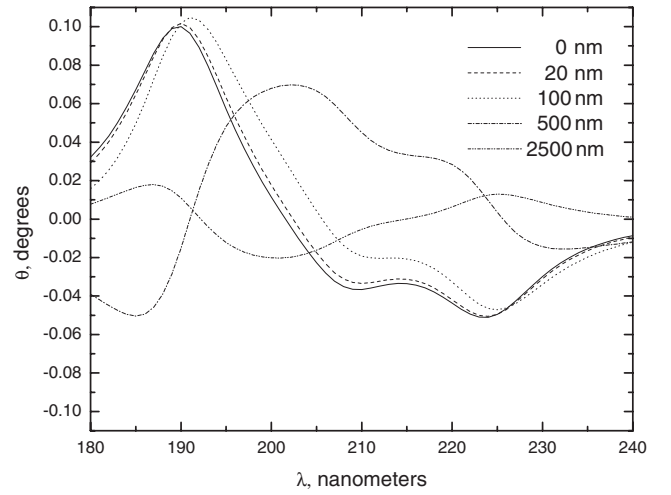


Figure 4. The same as in figure 3, but for spectra $\theta(\lambda)$.

Generally, we have for large values of $b \rightarrow \infty$: $\varphi(\lambda) \rightarrow 0$ and $\theta(\lambda) \rightarrow 0$. This means that the information, contained in initial spectra is lost due to the light scattering process. However, at small and intermediate values of b the situation is not so hopeless (see figures 3 and 4) and information on the arrangement of chemical groups for substances condensed inside small particles, which is responsible for the particular shapes of spectra $\varphi_0(\lambda)$ and $\theta_0(\lambda)$, can be retrieved in principle. For this, one needs to have an additional information on the shape, size and internal structure of particles under study.

5. Conclusion

The influence of the shape of particles on the circular dichroism and optical rotatory dispersion spectra of turbid layers was studied. The investigation was performed in the framework of the van de Hulst approximation [5], which is valid for optically soft ($|m - 1| \ll 1$) large ($ka \gg 1$) particles. It was found that intrinsic spectra $\Psi_0(\lambda)$ are related to measured spectra $\Psi(\lambda)$ by equation (15), where the function $H(\lambda)$ is given by integral (16) for particles of any shapes. The function $\xi(q)$ in equation (16) depends on the shape of particles. It is equal to 1 and $1.5\sqrt{1-q}$ for oriented cylinders and ellipsoids respectively. The dependence $\xi(q)$ for irregularly shaped particles does not

have such a simple analytical form. However, this function can be calculated numerically due to the fact that the product $l\xi(q)$ has a simple geometrical meaning. This is the length of a ray inside of a particle.

A major conclusion is that intrinsic CD $\theta_0(\lambda)$ and ORD $\varphi_0(\lambda)$ spectra of substances bounded inside optically soft large particles differ considerably from those measured for turbid layers. This difference disappears only for small phase shifts [6].

The results presented in this paper can be used for the development of chiroptical spectroscopy of biological media [9–12].

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